

Does the isotope effect of mercury support the BCS theory?

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In this paper, we reexamine the results of isotope effect experiments of the conventional monoatomic superconductor (Hg). It is shown clearly that the isotopic coefficients of mercury can be largely deviated from $\alpha = 0.5$, the standard value suggested by the phonon-mediated BCS pairing theory. According to the reported experimental results of various mercury isotopes, a giant isotope effect ($\alpha = 2.896$) is numerically found in the data. This study indicates that the validity of the conventional BCS theory cannot be verified by the isotope effect.

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In the field of superconductivity, the isotope effect has been considered can play the role in unraveling the microscopic superconducting mechanism. Historically, the discovery of the isotope effect in mercury in 1950 was immediately raised to the question regarding the coupling of the electrons to the lattice vibrations in the superconductor[1, 2]. It was widely believed that the isotope effect may relate to the origin of the effective attractive interaction between the repulsive electrons, which leads to the occurrence of superconductivity as suggested by the BCS pairing theory[3]. In the framework of BCS pairing theory, it was predicted that there would be a universal isotopic coefficient $a = 0.5$ for any superconductors[3]. The condensed matter physicists concluded that this prediction of the BCS theory was in good agreement with the reported isotope effects in some conventional superconductors (e.g., Hg, Sn and Pb)[4].

The experimental facts show that the isotope effect of the vast majority of superconductors (both conventional and non conventional) largely deviates from the standard value 0.5 of BCS theory[6–10]. For the conventional monoatomic superconductors, one notes that some superconductors have a negligible coefficient $\alpha_{Zr} \simeq 0$, while there are some reports on the inverse isotopic coefficients[6], for example, $\alpha_U = -2$ for the uranium element[8]. The inverse isotope effect has also been observed in numerous organic superconductors[10]. For the high-temperature superconductors, the isotope effect can have coefficients both smaller and larger than 0.5 depending on the doping levels. One notes that the cuprate superconductor $YBa_2Cu_3O_{7-y}$ has a very small oxygen isotope effect $\alpha = 0.0 \pm 0.027$ under the temperature of about 90 Kelvin[9]. Recently, the so-called large iron isotope effect was reported in the newly discovered iron-based $SmFeAsO_{1-x}F_x$ and $Ba_{1-x}K_xFe_2As_2$ superconductors[7].

In this letter, we will argue for the first time that the well-accepted isotopic coefficient of mercury in fact is not equal to 1/2. It will be shown that the maximum isotopic coefficient of mercury can reach as high as 2.896, a value

that is about six times of the value predicted by BCS theory and widely reported in the related papers. This result indicates that the relationship between the critical temperature T_c the isotopic mass M is much more complicated than that of the BCS theory. It seems most likely that the value of the isotopic coefficient does not directly lead to any priori conclusion about the pairing mechanism of the superconductivity. In other words, the BCS theory of the electron-phonon interaction mechanism not only cannot explain the isotope effect of the non-conventional superconductors, in fact, it also cannot explain the isotope effect observed in the conventional systems.

In the framework of BCS pairing theory, the superconducting critical temperature T_c is given by

$$k_B T_c = 1.13 \hbar \omega_D \exp \left(-\frac{1}{VN(E_F)} \right), \quad (1)$$

where ω_D is the Debye frequency, V is the electron-phonon interaction strength and $N(E_F)$ is the electronic density of states at the Fermi surface.

Eq. (1) is considered as one of the most significant and influential predictions of the BCS theory. In the harmonic approximation, both V and $N(E_F)$ are independent of the ionic mass, while the characteristic frequency ω_D can be expressed as

$$\omega_D \propto \frac{1}{\sqrt{M}}, \quad (2)$$

where M is the ionic mass.

By the combination of Eq. (1) and Eq. (2), it is not difficult to conclude that if the product $VN(E_F)$ is increased, then the T_c will rise. Moreover, using light elements M can raise the Debye frequency ω_D , and this in turn enhances the T_c of the corresponding superconductors. Based on the above two equations, BCS predicted a maximum T_c of around 30K for any superconductors which has been proven wrong since the discovery of the high- T_c oxide superconductors by Bednorz and Müller in 1986[11].

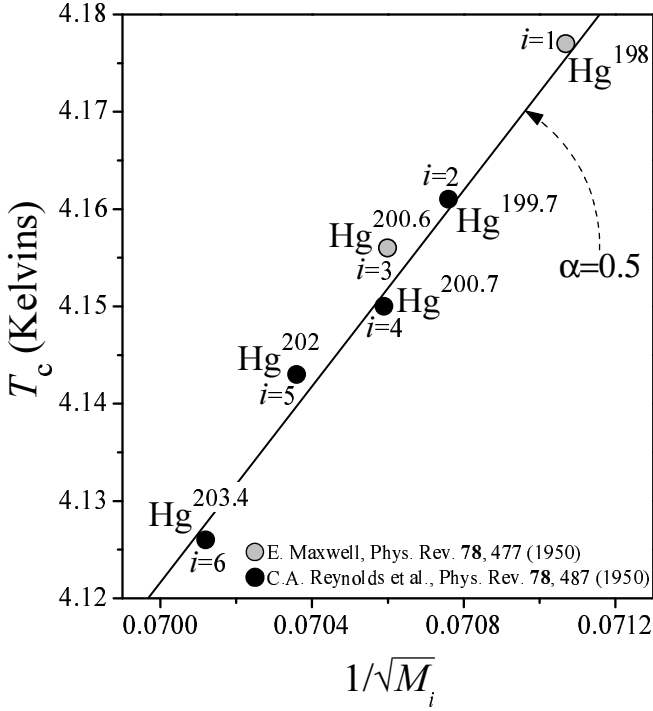


Figure 1: The experimental results of superconducting transition temperature as a function of isotopic mass for the elemental mercury.

Within the framework of the electron-phonon mechanism, the T_c can be described by the following relation:

$$T_c = AM^{-\alpha} \quad (3)$$

where A is a constant, M is the mass of the element substituted by its isotope and α is the so-called isotope coefficient which is defined as

$$\alpha = -\frac{\partial \ln T_c}{\partial \ln M} \simeq -\frac{M}{T_c} \frac{\Delta T_c}{\Delta M}, \quad (4)$$

where ΔT_c is the shift of the critical temperature and ΔM is the difference between the two isotopic mass.

In the standard BCS theory, T_c is inversely proportional to the square root of the masses of the isotopic elements, hence the isotope-effect coefficient $\alpha = 0.5$ which has been considered in good agreement with the experimental results in some non-transition metal superconductors, such as Hg, Sn and Pb. In the following discussion, we will show that this well-known conclusion is evidently wrong.

The superconductivity was first observed in mercury by Onnes in 1911[12]. Later, the isotope effects for mercury had been intensively investigated and its isotope-effect was claimed to be around $1/2$, as shown in Fig. 1. These results were the basis and foundation of the electron-phonon mechanism of BCS theory. And now, in order to illustrate the validity of the BCS theory, the

Table I: The reported superconducting transition temperature $T_c(i)$ of mercury with an isotopic mass of M_i . Moreover, α_i and β_i are newly defined parameters of isotope-effect coefficient and the percent error, respectively.

$Hg(i)$	1	2	3	4	5	6
M_i	198.0	199.7	200.6	200.7	202.0	203.4
$T_c(i)$	4.177	4.161	4.156	4.150	4.143	4.126
α_i	0.446	0.267	2.896	0.260	0.592	
β_i	10.8	46.6	479.2	48.0	18.4	

figure has been widely adopted in the textbooks of superconductivity.

Now let us begin our study of the relationship between the isotope effect and the BCS theory. For the sake of convenience of discussion in this letter, the isotopic masses M_i and the corresponding superconducting transition temperatures $T_c(i)$ are listed in the table below. It became obvious that only for the purpose of demonstrating the correctness of the prediction $\alpha = 0.5$ of BCS theory, the researchers intentionally selected special isotopic samples (1 and 6) and the isotope-effect coefficient was calculated by

$$\alpha = -\frac{M_1}{T_c(1)} \left[\frac{T_c(6) - T_c(1)}{M_6 - M_1} \right] \approx 0.448. \quad (5)$$

With the two sets of data $(T_c(1), M_1)$ and $(T_c(6), M_6)$, one indeed can obtain the desired isotope value close to $1/2$, but this is completely wrong. Mathematically, to apply Eq. (4) to estimate the parameter α , the variable quantities ΔT_c and ΔM must be infinitesimal. Hence, the calculation formula (5) holds only when ΔT_c and ΔM satisfy a linear relationship which is obviously not consistent with Eq. (3). Here, it is argued that a more accurate formula for calculating the isotope-effect coefficient would be

$$\begin{aligned} \alpha_i &\approx -\frac{\ln T_c(i+1) - \ln T_c(i)}{\ln M_{i+1} - \ln M_i} \\ &\approx -\frac{M_i}{T_c(i)} \frac{T_c(i+1) - T_c(i)}{M_{i+1} - M_i}. \end{aligned} \quad (6)$$

In the above formula, two sets of adjacent data $(T_c(i), M_i)$ and $(T_c(i+1), M_{i+1})$ are applied in the numerical simulation. We have argued that for a given superconductor, its isotope-effect coefficient may be completely different. This argument is well confirmed by directly putting the reported experimental results of Fig. 1 into Eq. (6), as shown in Table I. It is not difficult to find that all the obtained α_i are very different from 0.5 (in the range from 0.2 to 3), surprisingly, a giant isotope effect ($\alpha = 2.896$) which is about six times higher than the value $1/2$ suggested by BCS theory. In order to better present the deviation of the experimental results from the

BCS theory, we define the percent error β_i as:

$$\beta_i = \frac{|\alpha_i - 0.5|}{0.5} \times 100\%. \quad (7)$$

where 0.5 is the full isotope effect in the framework of BCS theory.

As also shown in Table I, the minimum percent error of the isotope coefficient for the elemental mercury is about 10.8%, while the maximum percent error can reach an inconceivable value of 479.2%. These results imply that the validity of the full isotope effect ($\alpha = 0.5$) of BCS pairing theory has never been experimentally verified. It is a possibility that the electron-phonon interaction based BCS theory may be fundamentally flawed.

In this short letter, we have presented arguments against the mainstream view that the isotope effect in the non-transition metal superconductor (Hg) is equal to 1/2, which is the characteristic value predicted by the classical form of BCS theory. It has been pointed out that the traditional method of calculation used to estimate superconducting isotope effect is mathematically unreliable. Based on the reported experimental result, very different isotope coefficients ranged from 0.267 to 2.896 for the mercury have been numerically obtained by using the improved method. Our results imply that the dependence of the critical temperature for superconductivity upon the isotopic mass was much more complicated than the BCS theory previously advocated. In our

opinion, the isotope effect cannot be applied as the direct evidence of the proposed electron-phonon coupling mechanism.

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